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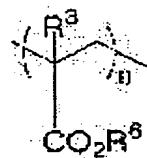
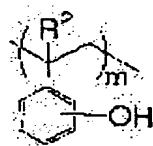
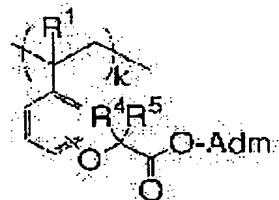
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(54) RESIST COMPOSITION

(57)Abstract:

PURPOSE: To improve resist characteristics such as light transmissivity, sensitivity, resolution and etching resistance, etc., by incorporating a polymer containing a specific structural unit and a radiosensitive component producing an acid by being irradiated with activated radioactive ray.

CONSTITUTION: This resist composition contains the polymer containing the structural unit expressed by formulae I-III and the radiosensitive component producing the acid by being irradiated with activated radioactive ray. In formulae I-III, each of R₁-R₃ is individually hydrogen atom, 1-4C substitutable alkyl group, halogen atom, cyano group or nitro group, each of R₄ and R₅ is individually hydrogen atom, 1-8C linear, branched or cyclic substitutable alkyl group, substitutable alkenyl group or substitutable aryl group, Adm is a 1-adamantyl group and R₆ is an acid unstable group. In each formula, (k), (m) and (n) respectively represent the ratio of each structural unit and are $0.05 \leq k \leq 0.95$, $0.1 \leq m \leq 0.95$, $0.05 \leq n \leq 0.6$ in $k+m+n=1$.



LEGAL STATUS

[Date of request for examination]

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* NOTICES *

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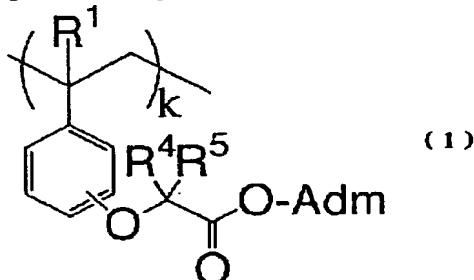
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CLAIMS

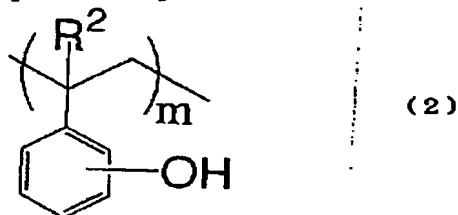
[Claim(s)]

[Claim 1] (2) 2 [a general formula (1) and] Reach (3).

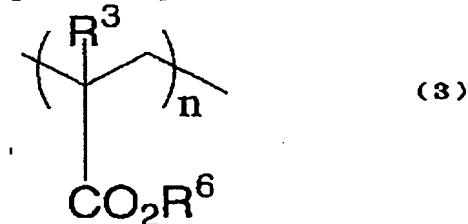
[Formula 1]



[Formula 2]



[Formula 3]



(As for R^1-R^3 , a hydrogen atom, the permutation good alkyl group of carbon numbers 1-4, a halogen atom, a cyano group, a nitro group, and R^4 and R^5 are a hydrogen atom, a straight chain, branching or the annular permutation good alkyl group of carbon numbers 1-8, a permutation good alkenyl radical, and a permutation good aryl group independently among formula (1) - (3), respectively, and Adm is 1-adamanthyl radical and R^6 is an acid instability radical.) k , m , and n in each formula express the rate of each configuration unit, and are $0.05 \leq k \leq 0.95$, $0.1 \leq m \leq 0.95$, and $0.05 \leq n \leq 0.6$ at the time of $k+m+n=1$. Resist constituent characterized by including the radiation sensitivity component which will generate an acid if the polymer and activation radiation containing the structural unit expressed irradiate.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the admiration radiation nature constituent suitable as a useful resist for the micro-machining of the semiconductor device using a radiation called charged-particle lines, such as far ultraviolet rays, such as an excimer laser, an X-ray, and an electron ray, in more detail about an admiration radiation constituent.

[0002]

[Description of the Prior Art] When manufacturing a semiconductor device, therefore, the image has been obtained on the lithography technique which applies a resist to a silicon wafer front face, builds a film, irradiates light, forms a latent image, subsequently develops it and forms the image of a negative or a positive. By the way, IC, LSI, and the technique that forms a detailed pattern 0.5micro or less in VLSI with high integration of a semi-conductor, densification, and a miniaturization further are demanded. However, it is very difficult to be accurate and to form a detailed pattern 0.5 micrometers or less in the conventional lithography using a near ultraviolet ray and a visible ray, and it is remarkable. [of a fall of the yield] For this reason, in order to change to the conventional photolithography using near ultraviolet ray light with a wavelength of 350-450nm and to raise the resolution of exposure, the lithography technique of using short far ultraviolet rays (ultraviolet C), a krypton-fluoride laser (KrF excimer laser light; wavelength of 248nm), an electron ray of wavelength, etc. is studied. Although novolak resin is used for the lithography using the conventional near ultraviolet ray light as a base material giant molecule, the trouble from which sensibility with this resin sufficient since permeability gets worse from that of a good thing extremely to far ultraviolet rays and KrF excimer laser light of short wavelength, when the permeability to ultraviolet-rays light with a wavelength of 350-450nm uses novolak resin as a base material giant molecule is not obtained that a pattern configuration is bad is known. for the purpose which improves the badness of transmission, the chemistry multiplier system resist using a polyvinyl phenol derivative as a base material giant molecule is examined -- **** (JP,2-27660,B) -- a pattern configuration has still come to satisfy a demand Moreover, the approaches (JP,5-249673,A etc.) using the hydrogenation polyvinyl phenol derivative aiming at raising transmission more as a base material macromolecule are learned as latest example. Although the pattern configuration has improved very much by this amelioration, the further improvement is called for from the demand characteristics especially definition, and etching-proof nature of the resist developed more.

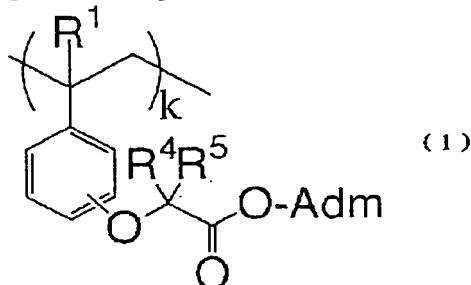
[0003]

[Problem(s) to be Solved by the Invention] Under this conventional technique, artificers were using the polymer which has the vinyl phenol unit which introduced the vinyl phenol unit and 1-adamantyloxy carbonyl group other than the methacrylate unit which introduced a certain kind of acid instability radical, as a result of inquiring wholeheartedly that the aforementioned problem should be solved, and it finds out that the resist constituent which was excellent at transparency, a dissolution deterrent, and etching-proof nature is obtained, and came to complete this invention based on this knowledge.

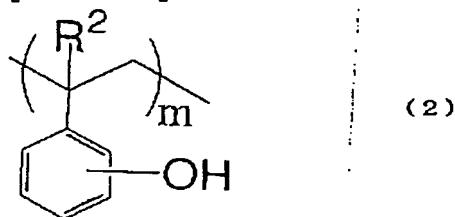
[0004]

[Means for Solving the Problem] (2) 2 [a general formula (1) and] In this way, according to this invention, reach (3).

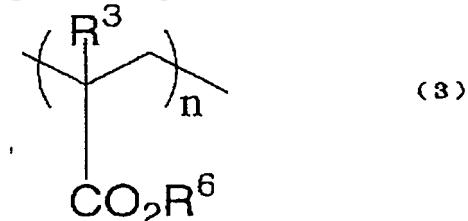
[Formula 4]



[Formula 5]



[Formula 6]



(As for R1–R3, a hydrogen atom, the permutation good alkyl group of carbon numbers 1–4, a halogen atom, a cyano group, a nitro group, and R4 and R5 are a hydrogen atom, a straight chain, branching or the annular permutation good alkyl group of carbon numbers 1–8, a permutation good alkenyl radical, and a permutation good aryl group independently among formula (1) – (3), respectively, and Adm is 1-adamanthyl radical and R6 is an acid instability radical.) k, m, and n in each formula express the rate of each configuration unit, and are 0.05<=k<=0.95, 0.1<=m<=0.95, and 0.05<=n<=0.6 at the time of k+m+n=1. An exposure of the polymer and activation radiation containing the structural unit expressed offers the resist constituent characterized by including the radiation sensitivity component which generates an acid.

[0005] Hereafter, this invention is explained in full detail. The polymer used by this invention is a polymer containing the configuration unit expressed with said formula (1) – (3). This polymer may be a block copolymer or may be a random copolymer. the weight average molecular weight of this polymer -- a minimum -- usually -- 1,000 -- desirable -- 2,000 -- it is -- an upper limit -- usually -- 100,000 -- it is 20,000 preferably. When it separates from this range, definition may fall. Halogen atom; cyano groups, such as a substitution product; fluorine with which one or more hydrogen atoms of the alkyl groups of the carbon numbers 1–4, such as a hydrogen atom; methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, s-butyl, and t-butyl, or these alkyl groups were permuted by the halogen atom, the alkoxy group, etc. as an example of R1–R3 in formula (1) – (3), chlorine, a bromine, and iodine; a nitro group is mentioned. It will not be restricted, especially if R6 is an acid instability radical and it is the radical decomposed with an acid in a formula (3). A 1-alkyl cycloalkyl radical like t-butyl, a 3rd class alkyl group; 1-methyl cyclopentylic group like t-amyl group, 1-methylcyclohexyl radical, 1-methyl cycloheptyl radical, and 1-ethyl Sickle hexyl as an example of such an acid instability radical; permutation allyl groups, such as a 1 and 1-dimethyl-2-propenyl radical, 2-butenyl group, and a 3-methyl-2-

butenyl group, etc. are illustrated.

[0006] The rate of the structural unit expressed with a formula (1), (2), and (3) is expressed with k, m, and n. The fall of sensibility happens and is not desirable, if the dissolution suppression effectiveness of the structural unit expressed with a formula (1) as opposed to [when there is comparatively little k] etching-proof nature and an alkali developer is not fully acquired but there is conversely. [much] Since the solubility of the resist unexposed section [as opposed to / when many / conversely / too / if there is comparatively little m, etching-proof nature will fall, and / a developer] of the structural unit expressed with a formula (2) increases, it is not desirable also when it is any. Since the fall of the sensibility by decline in transmission if there is comparatively little n and definition of the structural unit expressed with a formula (3) takes place, and the fall of etching-proof nature will take place if many [conversely], it is not desirable. the structural unit expressed with each type (1), (2), and (3) -- comparatively -- k, m, and n -- the time of $k+m+n=1$ -- usually -- $0.05 \leq k \leq 0.95$ and $0.1 \leq m \leq 0.95$ and $0.05 \leq n \leq 0.6$. the structural unit expressed with a formula (1) -- a minimum is usually 10% or more preferably 5% or more, and the upper limit of the rate in the resin of k is usually 60% or less preferably 95% or less comparatively. the structural unit expressed with a formula (2) -- a minimum is usually 30% or more preferably 10% or more, and the upper limit of the rate in the resin of m is usually 70% or less preferably 95% or less comparatively. the structural unit expressed with a formula (3) -- a minimum is usually 10% or more preferably 5% or more, and the upper limit of the rate in the resin of n is usually 50% or less preferably 60% or less comparatively. Moreover, both rate of being expressed with $k/(k+m)$ about the structural unit expressed with a formula (1) and the structural unit expressed with a formula (2) is $0.1 \leq k/(k+m) < 1$. the minimum of this rate $k/(k+m)$ -- usually -- 0.1 or more -- desirable -- 0.15 or more -- more -- desirable -- 0.2 or more -- it is -- an upper limit -- usually -- it is 0.7 or less more preferably 0.8 or less less than one. When there are too few these rates, the dissolution suppression effectiveness may fall, and it may lead to decline in a remaining rate of membrane, there is a possibility that an adhesive property may fall if there are too many these rates conversely, and neither is desirable. Furthermore, structural units (henceforth other structural units) other than the structural unit expressed with said formula (1) - (3) may exist in a polymer in the range which does not spoil the effectiveness of this invention. It comes out of the range which does not spoil the effectiveness of this invention said here in the polymer of other structural units comparatively, and an upper limit is usually 10% preferably 20%.

[0007] The polymer containing the structural unit expressed with said formula (1) - (3) used as a resinous principle by this invention is compounded according to a conventional method. For example, after carrying out the polymerization of the monomer which gives the structural unit of a formula (2) besides the approach of mixing and carrying out the polymerization of the monomer which gives the structural unit expressed with each type, and other structural units at a desired rate, and the monomer which gives the structural unit of a formula (3), there is also the approach of introducing 1-adamantyloxy carbonyl group into the phenolic hydroxyl group of a formula (2). Moreover, what carried out partial hydrogenation can use the obtained polymer by this invention.

[0008] As an example of a monomer of giving the structural unit of said formula (1), styrene derivatives and these alpha-methyl-styrene derivatives, such as 4-(1-adamantyloxy carbonyl methyloxy) styrene, 3-(1-adamantyloxy carbonyl methyloxy) styrene, and 2-(1-adamantyloxy carbonyl methyloxy) styrene, can be mentioned. As an example of a monomer of giving the structural unit of said formula (2), 4-hydroxystyrene, 3-hydroxystyrene, 2-hydroxystyrene, alpha-methyl-4-hydroxystyrene, alpha-methyl-3-hydroxystyrene, alpha-methyl-2-hydroxystyrene, 4-hydroxy-3-methyl styrene, etc. are illustrated. As an example of a monomer of giving the structural unit of said formula (3), acrylic ester (meta), such as acrylic-acid (meta) t-butyl, acrylic-acid (meta) t-amyl, and acrylic-acid (meta) 1-methylcyclohexyl, is illustrated.

[0009] Moreover, what is necessary is just to make compounds, such as bromoacetic acid 1-adamanthyl, chloroacetic-acid 1-adamanthyl, and alpha-bromopropionic acid 1-adamanthyl, react under basic conditions to the polymer of the monomer which gives said formula (2) and formula (3), when introducing 1-adamantyloxy carbonyl group of a formula (1) later.

[0010] As an example of the resin used by this invention, they are 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / t-butyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / t-amyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl chil oxy-) styrene / 4-hydroxystyrene / 1-methyl cyclopentyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 1-methylcyclohexyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 1-methyl cycloheptyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 1-ethyl cyclohexyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 1, and 1-dimethyl-2-propenyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 2-but enyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 3-methyl-2-but enyl A methacrylate polymer etc. is illustrated.

[0011] If the acid generator (henceforth PAG) used in this invention is matter which generates Broensted acid or Lewis acid when it is exposed by the activation radiation, especially a limit does not have it and well-known things, such as an onium salt, a halogenation organic compound, a quinone diazide compound, alpha, alpha screw (sulfonyl) diazomethane system compound, an alpha-carbonyl-alpha-sulfonyl diazomethane system compound, a sulfone compound, an organic-acid ester compound, an organic-acid amide compound, and an organic-acid imide compound, can be used for it. As an onium salt, sulfonium salt, such as iodonium salt, such as diazonium salt, ammonium salt, and diphenyliodonium triflate, and triphenylsulfonium triflate, phosphonium salt, arsonium salt, oxonium salt, etc. are mentioned.

[0012] As a halogenation organic compound, a halogen content OKISA diazole system compound, A halogen content triazine system compound, a halogen content acetophenone system compound, A halogen content benzophenone system compound, a halogen content sulfo KISAIDO system compound, A halogen content sulfone system compound, a halogen content thiazole system compound, A halogen content oxazole system compound, a halogen content triazole compound, A halogen content 2-pyrone system compound, other halogen content heterocycle-like compounds, A halogen content aliphatic hydrocarbon compound, a halogen content aromatic hydrocarbon compound, a sulphenyl halide compound, etc. are mentioned. Specifically Tris (2, 3-dibromopropyl) phosphate, tris (2, 3-dibromo-3-chloropropyl) phosphate, Tetrabromo chloro butane, hexachlorobenzene, hexabromobenzene, A hexa BUROMO cyclo dodecane, hexabromobiphenyl, allyl compound TORIBUROMO phenyl ether, The screw (chloro ethyl) ether of tetra-chloro bisphenol A, tetrabromobisphenol A, and tetra-chloro bisphenol A, The screw (BUROMO ethyl) ether of tetrabromobisphenol A, the screw (2, 3-dichloro propyl) ether of bisphenol A, The screw (2, 3-dibromopropyl) ether of bisphenol A, the screw (2, 3-dichloro propyl) ether of tetra-chloro bisphenol A, The screw (2, 3-dibromopropyl) ether of tetrabromobisphenol A, The screw (chloro ethyl) ether of the tetra-chloro bisphenol S, the tetrabromo bisphenol S, and the tetra-chloro bisphenol S, The screw (BUROMO ethyl) ether of the tetrabromo bisphenol S, the screw (2, 3-dichloro propyl) ether of Bisphenol S, The screw (2, 3-dibromopropyl) ether of Bisphenol S, tris (2, 3-dibromopropyl) isocyanurate, 2 and 2-screw (4-hydroxy - 3, 5-dibromo phenyl) propane, Halogen system flame retarders and dichlorodiphenyltrichloroethane, such as 2 and 2-screw (4-(2-hydroxy ethoxy)-3, 5-dibromo phenyl) propane, Pentachlorophenol, 2 and 4, 6-TORIKURORO phenyl 4'-nitrophenyl ether, 2, 4-dichlorophenyl 3' - methoxy -4'-nitrophenyl ether, Acetic acid, 4, 5 and 6, 7-tetra-chloro phthalide, 1 and 1-screw (4-chlorophenyl) ethanol, 1, and 1-screw (4-chlorophenyl) - 2, 2, and 2-trichloroethanol, Organic chloro system agricultural chemicals, such as 2, 4, 4', a 5-tetra-chlorodiphenyl sulfide, 2 and 4, 4', and a 5-tetra-chlorodiphenyl sulfone, etc. are illustrated.

[0013] As an example of a quinone diazide compound, 1, a 2-benzoquinone diazido-4-sulfonate, 1, a 2-naphthoquinonediazide-4-sulfonate, 1, a 2-naphthoquinonediazide-5-sulfonate, The sulfonate of a quinone diazide derivative like a 2, 1-naphthoquinonediazide-4-sulfonate, 2, and 1-benzoquinone diazido-5-sulfonate, and 1, 2-benzoquinone-2-diazido-4-sulfonic-acid chloride, 1,2-naphthoquinone-2-diazido-4-sulfonic-acid chloride, 1,2-naphthoquinone-2-diazido-5-sulfonic-acid chloride, The sulfonic-acid chloride of quinone diazide derivatives, such as 1,2-naphthoquinone-1-diazido-6-sulfonic-acid chloride, 1, and 2-benzoquinone-1-diazido-5-

sulfonic-acid chloride, etc. is mentioned.

[0014] As alpha and an alpha screw (sulfonyl) diazomethane system compound, alpha, alpha screw (sulfonyl) diazomethane, etc. which have un-permuting, the alkyl group permuted symmetrically or asymmetrically, an alkenyl radical, an aralkyl radical, an aromatic series radical, or a heterocycle-like radical are mentioned. As an example of an alpha-carbonyl-alpha-sulfonyl diazomethane system compound, the alpha-carbonyl-alpha-sulfonyl diazomethane which has un-permuting, the alkyl group permuted symmetrically or asymmetrically, an alkenyl radical, an aralkyl radical, an aromatic series radical, or a heterocycle-like radical is mentioned. As an example of a sulfone compound, a sulfone compound, a disulfon compound, etc. which have un-permuting, the alkyl group permuted symmetrically or asymmetrically, an alkenyl radical, an aralkyl radical, an aromatic series radical, or a heterocycle-like radical are mentioned.

[0015] As organic-acid ester, carboxylate, a sulfonate, phosphoric ester, etc. are mentioned, as an organic-acid amide, carboxylic amide, a sulfonic-acid amide, a phosphoric-acid amide, etc. are mentioned, and carboxylic-acid imide, sulfonic-acid imide, phosphoric-acid imide, etc. are mentioned as organic-acid imide.

[0016] These PAG may be used independently, or two or more kinds may be mixed and used for it. the resin 100 weight section which uses the loadings of these PAG by this invention -- receiving -- a minimum -- usually -- the 0.01 weight section -- desirable -- the 0.2 weight section -- it is -- an upper limit -- usually -- 50 weight sections -- they are 30 weight sections preferably. Formation of a pattern is an impossible next door under in the 0.01 weight section. If 50 weight sections are exceeded, that it is easy to generate ******, it will become or the problem of a pattern configuration getting worse will arise, and also when it is any, it is not desirable on the engine performance of a resist.

[0017] In this invention, it is made to dissolve in a solvent and the resist constituent which consists of said resin and PAG is used. What is generally used as a solvent for resist constituents can be used for a solvent. As an example Ketones;n-propanol, such as an acetone, a methyl ethyl ketone, a cyclohexanone, and cyclopentanone, i-propanol, n-butanol, i-butanol, t-butanol, Alcohols, such as a cyclohexanol; Ethylene glycol wood ether, Ether, such as ethylene glycol diethylether and dioxane; Ethylene glycol wood ether, Ethylene glycol monoethyl ether, propylene glycol monomethyl ether, Alcoholic ether, such as the propylene glycol monoethyl ether; Formic-acid propyl, Formic-acid butyl, propyl acetate, butyl acetate, methyl propionate, ethyl propionate, Ester;alpha-oxy-methyl propionates, such as methyl butyrate and ethyl butylate, alpha-oxy-ethyl propionate, 2-methoxy methyl propionate, Hydroxy acid ester, such as 2-methoxy ethyl propionate; A cellosolve acetate, Methyl-cellosolve acetate, ethylcellosolve acetate, a propyl cellosolve acetate, Cellosolve ester, such as butyl-cellosolve acetate; Propylene glycol, Propylene-glycol-monomethyl-ether acetate, propylene glycol monoethyl ether acetate, Propylene glycols, such as the propylene glycol monobutyl ether; The diethylene GIRIKORU monomethyl ether, Diethylene glycol monoethyl ether, diethylene-glycol wood ether, diethylene-glycols [, such as diethylene-glycol diethylether,]; -- halogenated hydrocarbon [, such as a trichloroethylene,]; -- toluene -- Aromatic hydrocarbon, such as a xylene; polar solvents, such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl acetamide, and N-methyl pyrrolidone, etc. are illustrated, and these may mix and use independent or two kinds or more.

[0018] An additive with compatibility, such as what is generally added by the resist constituent as an additive, for example, a surfactant, a preservation stabilizer, a sensitizer, a striae SHON inhibitor, and a low-molecular phenolic compound, can be made to contain in this invention.

[0019] In the constituent of this invention, the solubility of an irradiated part changes in response to an operation of the acid which generates the polymer which has the configuration unit expressed with said formula (3) from an acid generator by the exposure of a radiation. The constituent of this invention acts as a positive resist by using an alkali developer. By making the structural unit expressed with a formula (1) and (2) exist in a polymer, resist properties, such as dry cleaning-proof dirty nature, light transmission nature, definition, and the dissolution suppression effectiveness, improve.

[0020] Although the resist constituent of this invention usually uses an alkali water solution as

an alkali developer As an example, a sodium hydroxide, a potassium hydroxide, a sodium silicate, The water solution of inorganic alkali, such as ammonia; The water-solution; diethylamine of primary amines, such as ethylamine and propylamine, The water solution of secondary amines, such as a dipropyl amine; The water-solution; diethyl ethanolamine of tertiary amines, such as a trimethylamine and triethylamine, The water solution of alcoholic amines, such as triethanolamine; Tetramethylammonium hydroxide, Tetraethylammonium hydroxide, trimethyl hydroxymethyl ammonium hydroxide, The water solution of quaternary ammonium hydroxide, such as triethyl hydroxymethyl ammonium hydroxide and trimethylhydroxyethylammonium hydroxide, etc. is mentioned. Moreover, water-soluble organic solvents, such as a methanol, ethanol, propanol, and ethylene glycol, a surfactant, the dissolution retardant of resin, etc. can be added in the above-mentioned alkali water solution if needed.

[0021] After applying the resist solution made to dissolve the resist constituent of this invention in a solvent to substrate front faces, such as a silicon wafer, with a conventional method, the resist film can be formed by carrying out desiccation removal of the solvent. Especially as the method of application at this time, the object for prizes of the spin coating is carried out. Thus, as a source of exposure used for the obtained resist film by the exposure for making a pattern form, sources of ionizing radiation, such as far ultraviolet rays, KrF excimer laser light, an X-ray, and an electron ray, are mentioned. Furthermore, by heat-treating after exposure (after [exposure] BEKU), a deprotection reaction is made to end and improvement and stabilization of sensibility can be attained.

[0022]

[Example] The example of reference, a synthetic example, and an example are given to below, and this invention is explained to it still more concretely. In addition, the section in each example and % are weight criteria as long as there is no notice especially.

[0023] (Synthetic example 1) 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / t-butyl Methacrylate polymer ** polymerization process 4-vinyl phenol 72.1g (0.60 mols), t-butyl Methacrylate 17.1g (0.12 mols), azobisisobutyronitril 1.5g (0.009 mols) and dioxane 150ml were taught to the 500ml flask, and stirring was performed at 80 degrees C under the nitrogen air current for 20 hours. The obtained reaction mixture was supplied to the 5l. xylene, and the produced precipitation was filtered. The obtained solid content was dissolved in diethylether 200ml, it supplied to 3l. n-hexane and the produced precipitation was filtered (reprecipitation actuation). After repeating this reprecipitation actuation 3 times, it dried and 26.3g 4-hydroxystyrene / t-butyl methacrylate polymer were obtained. The obtained polymer was Mw=5,130 as a result of GPC analysis. Moreover, the polymerization ratio of 4-hydroxystyrene / t-butyl methacrylate was 71/29 as a result of 1 H-NMR spectrum analysis.

[0024] ** 4-hydroxystyrene / 20.0g [of t-butyl methacrylate polymers], and acetone 150ml obtained by the qualification process point was taught and dissolved in 500ml flask. Bromoacetic acid 1-adamanthyl 6.2g (0.023 mols), 3.5g (0.025ml) of anhydrous potassium carbonate, and 4.2g (0.025 mols) of potassium iodide were added to this, and stirring was performed at 50 degrees C for 8 hours. After removing salts from the obtained reaction mixture, it supplied to 5l. n-hexane and the produced settling were filtered. The obtained solid content was dissolved in tetrahydrofuran 100ml, it supplied to the 5l. hexane and the produced precipitation was filtered (reprecipitation actuation). It dries, after repeating this reprecipitation actuation twice, and they are 18.8g 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / t-butyl. The methacrylate polymer was obtained. The obtained polymer was Mw=6,200 as a result of GPC analysis. Moreover, they are 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / t-butyl as a result of 1 H-NMR spectrum analysis. The polymerization ratio of methacrylate was 15/57/28.

[0025] (Synthetic example 2) 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / 1-methylcyclohexyl Methacrylate polymer ** polymerization process t-butyl It is 1-methylcyclohexyl instead of methacrylate. Except being referred to as methacrylate 29.1g (0.16 mols), it carried out like ** polymerization process of the synthetic example 1, and 22.7g 4-hydroxystyrene / 1-methylcyclohexyl methacrylate polymer were obtained. The obtained polymer was Mw=6,330 as a result of GPC analysis. Moreover, they are 4-hydroxystyrene / 1-

methylcyclohexyl as a result of 1 H-NMR spectrum analysis. The polymerization ratio of methacrylate was 65/35.

** 4-hydroxystyrene / 1-methylcyclohexyl obtained at said process as a qualification process polymer Except using methacrylate 20.0g, it carries out like ** qualification process of the synthetic example 1, and they are 18.0g 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / 1-methylcyclohexyl. The methacrylate polymer was obtained. The obtained polymer was Mw=7,300 as a result of GPC analysis. Moreover, they are 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / 1-methylcyclohexyl as a result of 1 H-NMR spectrum analysis. The polymerization ratio of methacrylate was 14/50/36.

[0026] (Synthetic example 3) 4-(1-adamanthyl OKISHISHI carbonyl methyloxy) styrene / 4-hydroxystyrene / 3-methyl-2-butene Methacrylate polymer ** polymerization process t-butyl It is 3-methyl-2-butene instead of methacrylate. Except being referred to as methacrylate 18.5g (0.12 mols), it carried out like ** polymerization process of the synthetic example 1, and 20.7g 4-hydroxystyrene / 3-methyl-2-butene methacrylate polymer was obtained. The obtained polymer was Mw=5,500 as a result of GPC analysis. Moreover, they are 4-hydroxystyrene / 3-methyl-2-butene as a result of 1 H-NMR spectrum analysis. The polymerization ratio of methacrylate was 75/25.

** 4-hydroxystyrene / 3-methyl-2-butene obtained at said process as a qualification process polymer Except using methacrylate 20.0g, it carries out like ** qualification process of the synthetic example 1, and they are 19.0g 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / 3-methyl-2-butene. The methacrylate polymer was obtained. The obtained polymer was Mw=6,400 as a result of GPC analysis. Moreover, they are 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / 3-methyl-2-butene as a result of 1 H-NMR spectrum analysis. The polymerization ratio of methacrylate was 16/59/25.

[0027] (Examples 1-4) The triphenylsulfonium triflate 5 section and the fluoroochemical surfactant 0.01 section were dissolved in the ethyl lactate 440 section as the polymer 100 section obtained in the above-mentioned synthetic examples 1-3, and an acid generator, it filtered with the 0.1-micrometer filter made from polytetrafluoroethylene (Millipore Corp. make), and the resist solution was prepared. After carrying out the spin coat of this resist solution on a silicon wafer, the resist film of 1.0 micrometers of thickness was formed by performing BEKU for 90 seconds at 110 degrees C. This wafer was exposed using REKUCHIRU for a test with the KrF excimer stepper (NA=0.45). Subsequently, after performing BEKU for 60 seconds at 90 degrees C, the tetramethylammonium hydroxide water solution performed the immersion phenomenon for 1 minute, and the positive type pattern was obtained. Definition when the good pattern obtained by fitness-ization of the sensibility of these resist film and exposure is shown is shown in Table 1. Furthermore, when the wafer by which pattern formation was carried out was etched using the dry etching system (the product made from Japanese ** Anelva, DEM451T) by power 300W, pressure 0.03Torr, gas CF₄/H₂, and frequency 13.56MHz, with the wafer using the polymer of the synthetic examples 1-3, it turned out that only the place which did not have a pattern is etched. Moreover, observation of the resist pattern after etching was maintaining the configuration before etching mostly.

[0028]

[Table 1]

実施例	樹脂		感度 (mJ/cm ²)	解像性 (μm)
	合成例	k / m / n		
1	1	15/57/28	0.208	1.7
2	2	14/50/36	0.219	1.8
3	3	16/59/26	0.213	2.0

[0029]

[Effect of the Invention] In this way, according to this invention, it excels in resist properties,

such as light transmission nature, sensibility, definition, and etching-proof nature, and the resist ingredient suitable for the lithography using short far ultraviolet rays and KrF excimer laser light of wavelength is obtained. Especially the resist constituent of this invention is suitable as a positive resist for micro processing of a semiconductor device.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] This invention relates to the admiration radiation nature constituent suitable as a useful resist for the micro-machining of the semiconductor device using a radiation called charged-particle lines, such as far ultraviolet rays, such as an excimer laser, an X-ray, and an electron ray, in more detail about an admiration radiation constituent.

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PRIOR ART

[Description of the Prior Art] When manufacturing a semiconductor device, therefore, the image has been obtained on the lithography technique which applies a resist to a silicon wafer front face, builds a film, irradiates light, forms a latent image, subsequently develops it and forms the image of a negative or a positive. By the way, IC, LSI, and the technique that forms a detailed pattern 0.5micro or less in VLSI with high integration of a semi-conductor, densification, and a miniaturization further are demanded. However, it is very difficult to be accurate and to form a detailed pattern 0.5 micrometers or less in the conventional lithography using a near ultraviolet ray and a visible ray, and it is remarkable. [of a fall of the yield] For this reason, in order to change to the conventional photolithography using near ultraviolet ray light with a wavelength of 350-450nm and to raise the resolution of exposure, the lithography technique of using short far ultraviolet rays (ultraviolet C), a krypton-fluoride laser (KrF excimer laser light; wavelength of 248nm), an electron ray of wavelength, etc. is studied. Although novolak resin is used for the lithography using the conventional near ultraviolet ray light as a base material giant molecule, the trouble from which sensibility with this resin sufficient since permeability gets worse from that of a good thing extremely to far ultraviolet rays and KrF excimer laser light of short wavelength, when the permeability to ultraviolet-rays light with a wavelength of 350-450nm uses novolak resin as a base material giant molecule is not obtained that a pattern configuration is bad is known. for the purpose which improves the badness of transmission, the chemistry multiplier system resist using a polyvinyl phenol derivative as a base material giant molecule is examined -- **** (JP,2-27660,B) -- a pattern configuration has still come to satisfy a demand Moreover, the approaches (JP,5-249673,A etc.) using the hydrogenation polyvinyl phenol derivative aiming at raising transmission more as a base material macromolecule are learned as latest example. Although the pattern configuration has improved very much by this amelioration, the further improvement is called for from the demand characteristics especially definition, and etching-proof nature of the resist developed more.

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EFFECT OF THE INVENTION

[Effect of the Invention] In this way, according to this invention, it excels in resist properties, such as light transmission nature, sensibility, definition, and etching-proof nature, and the resist ingredient suitable for the lithography using short far ultraviolet rays and KrF excimer laser light of wavelength is obtained. Especially the resist constituent of this invention is suitable as a positive resist for micro processing of a semiconductor device.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Under this conventional technique, artificers were using the polymer which has the vinyl phenol unit which introduced the vinyl phenol unit and 1-adamantyloxy carbonyl group other than the methacrylate unit which introduced a certain kind of acid instability radical, as a result of inquiring wholeheartedly that the aforementioned problem should be solved, and it finds out that the resist constituent which was excellent at transparency, a dissolution deterrent, and etching-proof nature is obtained, and came to complete this invention based on this knowledge.

[Translation done.]

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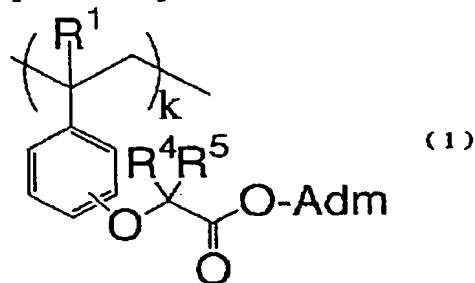
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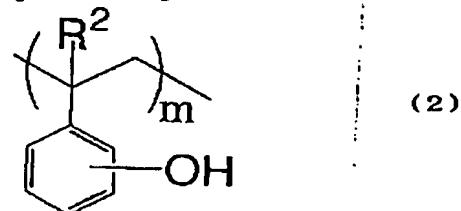
MEANS

[Means for Solving the Problem] (2) 2 [a general formula (1) and] In this way, according to this invention, reach (3).

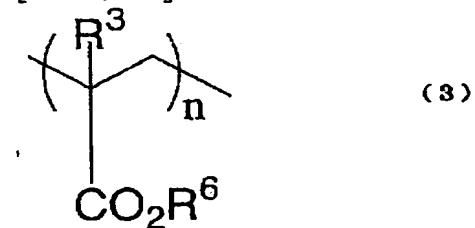
[Formula 4]



[Formula 5]



[Formula 6]



(As for R1–R3, a hydrogen atom, the permutation good alkyl group of carbon numbers 1–4, a halogen atom, a cyano group, a nitro group, and R4 and R5 are a hydrogen atom, a straight chain, branching or the annular permutation good alkyl group of carbon numbers 1–8, a permutation good alkenyl radical, and a permutation good aryl group independently among formula (1) – (3), respectively, and Adm is 1-adamanthyl radical and R6 is an acid instability radical.) k, m, and n in each formula express the rate of each configuration unit, and are $0.05 \leq k \leq 0.95$, $0.1 \leq m \leq 0.95$, and $0.05 \leq n \leq 0.6$ at the time of $k+m+n=1$. An exposure of the polymer and activation radiation containing the structural unit expressed offers the resist constituent characterized by including the radiation sensitivity component which generates an acid.

[0005] Hereafter, this invention is explained in full detail. The polymer used by this invention is a polymer containing the configuration unit expressed with said formula (1) – (3). This polymer may be a block copolymer or may be a random copolymer. the weight average molecular weight of

this polymer -- a minimum -- usually -- 1,000 -- desirable -- 2,000 -- it is -- an upper limit -- usually -- 100,000 -- it is 20,000 preferably. When it separates from this range, definition may fall. Halogen atom; cyano groups, such as a substitution product; fluorine with which one or more hydrogen atoms of the alkyl groups of the carbon numbers 1-4, such as a hydrogen atom; methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, s-butyl, and t-butyl, or these alkyl groups were permuted by the halogen atom, the alkoxy group, etc. as an example of R1-R3 in formula (1) - (3), chlorine, a bromine, and iodine; a nitro group is mentioned. It will not be restricted, especially if R6 is an acid instability radical and it is the radical decomposed with an acid in a formula (3). A 1-alkyl cycloalkyl radical like t-butyl, a 3rd class alkyl group; 1-methyl cyclopentylic group like t-amyl group, 1-methylcyclohexyl radical, 1-methyl cycloheptyl radical, and 1-ethyl Sickle hexyl as an example of such an acid instability radical; permutation allyl groups, such as a 1 and 1-dimethyl-2-propenyl radical, 2-butenyl group, and a 3-methyl-2-butenyl group, etc. are illustrated.

[0006] The rate of the structural unit expressed with a formula (1), (2), and (3) is expressed with k, m, and n. The fall of sensibility happens and is not desirable, if the dissolution suppression effectiveness of the structural unit expressed with a formula (1) as opposed to [when there is comparatively little k] etching-proof nature and an alkali developer is not fully acquired but there is conversely. [much] Since the solubility of the resist unexposed section [as opposed to / when many / conversely / too / if there is comparatively little m, etching-proof nature will fall, and / a developer] of the structural unit expressed with a formula (2) increases, it is not desirable also when it is any. Since the fall of the sensibility by decline in transmission if there is comparatively little n and definition of the structural unit expressed with a formula (3) takes place, and the fall of etching-proof nature will take place if many [conversely], it is not desirable. the structural unit expressed with each type (1), (2), and (3) -- comparatively -- k, m, and n -- the time of $k+m+n=1$ -- usually -- $0.05 \leq k \leq 0.95$ and $0.1 \leq m \leq 0.95$ and $0.05 \leq n \leq 0.6$. the structural unit expressed with a formula (1) -- a minimum is usually 10% or more preferably 5% or more, and the upper limit of the rate in the resin of k is usually 60% or less preferably 95% or less comparatively. the structural unit expressed with a formula (2) -- a minimum is usually 30% or more preferably 10% or more, and the upper limit of the rate in the resin of m is usually 70% or less preferably 95% or less comparatively. the structural unit expressed with a formula (3) -- a minimum is usually 10% or more preferably 5% or more, and the upper limit of the rate in the resin of n is usually 50% or less preferably 60% or less comparatively. Moreover, both rate of being expressed with $k/(k+m)$ about the structural unit expressed with a formula (1) and the structural unit expressed with a formula (2) is $0.1 \leq k/(k+m) < 1$. the minimum of this rate $k/(k+m)$ -- usually -- 0.1 or more -- desirable -- 0.15 or more -- more -- desirable -- 0.2 or more -- it is -- an upper limit -- usually -- it is 0.7 or less more preferably 0.8 or less less than one. When there are too few these rates, the dissolution suppression effectiveness may fall, and it may lead to decline in a remaining rate of membrane, there is a possibility that an adhesive property may fall if there are too many these rates conversely, and neither is desirable. Furthermore, structural units (henceforth other structural units) other than the structural unit expressed with said formula (1) - (3) may exist in a polymer in the range which does not spoil the effectiveness of this invention. It comes out of the range which does not spoil the effectiveness of this invention said here in the polymer of other structural units comparatively, and an upper limit is usually 10% preferably 20%.

[0007] The polymer containing the structural unit expressed with said formula (1) - (3) used as a resinous principle by this invention is compounded according to a conventional method. For example, after carrying out the polymerization of the monomer which gives the structural unit of a formula (2) besides the approach of mixing and carrying out the polymerization of the monomer which gives the structural unit expressed with each type, and other structural units at a desired rate, and the monomer which gives the structural unit of a formula (3), there is also the approach of introducing 1-adamantyloxy carbonyl group into the phenolic hydroxyl group of a formula (2). Moreover, what carried out partial hydrogenation can use the obtained polymer by this invention.

[0008] As an example of a monomer of giving the structural unit of said formula (1), styrene

derivatives and these alpha-methyl-styrene derivatives, such as 4-(1-adamantyloxy carbonyl methoxy) styrene, 3-(1-adamantyloxy carbonyl methoxy) styrene, and 2-(1-adamantyloxy carbonyl methoxy) styrene, can be mentioned. As an example of a monomer of giving the structural unit of said formula (2), 4-hydroxystyrene, 3-hydroxystyrene, 2-hydroxystyrene, alpha-methyl-4-hydroxystyrene, alpha-methyl-3-hydroxystyrene, alpha-methyl-2-hydroxystyrene, 4-hydroxy-3-methyl styrene, etc. are illustrated. As an example of a monomer of giving the structural unit of said formula (3), acrylic ester (meta), such as acrylic-acid (meta) t-butyl, acrylic-acid (meta) t-amyl, and acrylic-acid (meta) 1-methylcyclohexyl, is illustrated. [0009] Moreover, what is necessary is just to make compounds, such as bromoacetic acid 1-adamanthyl, chloroacetic-acid 1-adamanthyl, and alpha-bromopropionic acid 1-adamanthyl, react under basic conditions to the polymer of the monomer which gives said formula (2) and formula (3), when introducing 1-adamantyloxy carbonyl group of a formula (1) later.

[0010] As an example of the resin used by this invention, they are 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / t-butyl. Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / t-amyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl chil oxy-) styrene / 4-hydroxystyrene / 1-methyl cyclopentyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 1-methylcyclohexyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 1-methyl cycloheptyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 1-ethyl cyclohexyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 1, and 1-dimethyl-2-propenyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 2-butenyl Methacrylate polymer, 4-(1-adamantyloxy carbonyl methoxy) styrene / 4-hydroxystyrene / 3-methyl-2-butenyl A methacrylate polymer etc. is illustrated.

[0011] If the acid generator (henceforth PAG) used in this invention is matter which generates Broensted acid or Lewis acid when it is exposed by the activation radiation, especially a limit does not have it and well-known things, such as an onium salt, a halogenation organic compound, a quinone diazide compound, alpha, alpha screw (sulfonyl) diazomethane system compound, an alpha-carbonyl-alpha-sulfonyl diazomethane system compound, a sulfone compound, an organic-acid ester compound, an organic-acid amide compound, and an organic-acid imide compound, can be used for it. As an onium salt, sulfonium salt, such as iodonium salt, such as diazonium salt, ammonium salt, and diphenyliodonium triflate, and triphenylsulfonium triflate, phosphonium salt, arsonium salt, oxonium salt, etc. are mentioned.

[0012] As a halogenation organic compound, a halogen content OKISA diazole system compound, A halogen content triazine system compound, a halogen content acetophenone system compound, A halogen content benzophenone system compound, a halogen content sulfo KISAIDO system compound, A halogen content sulfone system compound, a halogen content thiazole system compound, A halogen content oxazole system compound, a halogen content triazole compound, A halogen content 2-pyrone system compound, other halogen content heterocycle-like compounds, A halogen content aliphatic hydrocarbon compound, a halogen content aromatic hydrocarbon compound, a sulphenyl halide compound, etc. are mentioned. Specifically Tris (2, 3-dibromopropyl) phosphate, tris (2, 3-dibromo-3-chloropropyl) phosphate, Tetrabromo chloro butane, hexachlorobenzene, hexabromobenzene, A hexa BUROMO cyclo dodecane, hexabromobiphenyl, allyl compound TORIBUROMO phenyl ether, The screw (chloro ethyl) ether of tetra-chloro bisphenol A, tetrabromobisphenol A, and tetra-chloro bisphenol A, The screw (BUROMO ethyl) ether of tetrabromobisphenol A, the screw (2, 3-dichloro propyl) ether of bisphenol A, The screw (2, 3-dibromopropyl) ether of bisphenol A, the screw (2, 3-dichloro propyl) ether of tetra-chloro bisphenol A, The screw (2, 3-dibromopropyl) ether of tetrabromobisphenol A, The screw (chloro ethyl) ether of the tetra-chloro bisphenol S, the tetrabromo bisphenol S, and the tetra-chloro bisphenol S, The screw (BUROMO ethyl) ether of the tetrabromo bisphenol S, the screw (2, 3-dichloro propyl) ether of Bisphenol S, The screw (2, 3-dibromopropyl) ether of Bisphenol S, tris (2, 3-dibromopropyl) isocyanurate, 2 and 2-screw (4-hydroxy - 3, 5-dibromo phenyl) propane, Halogen system flame retarders and dichlorodiphenyltrichloroethane, such as 2 and 2-screw (4-(2-hydroxy ethoxy)-3, 5-dibromo

phenyl) propane, Pentachlorophenol, 2 and 4, 6-TORIKURORO phenyl 4'-nitrophenyl ether, 2, 4-dichlorophenyl 3'-methoxy-4'-nitrophenyl ether, Acetic acid, 4, 5 and 6, 7-tetra-chlorophthalide, 1 and 1-screw (4-chlorophenyl) ethanol, 1, and 1-screw (4-chlorophenyl)-2, 2, and 2-trichloroethanol, Organic chloro system agricultural chemicals, such as 2, 4, 4', a 5-tetra-chlorodiphenyl sulfide, 2 and 4, 4', and a 5-tetra-chlorodiphenyl sulfone, etc. are illustrated.

[0013] As an example of a quinone diazide compound, 1, a 2-benzoquinone diazido-4-sulfonate, 1, a 2-naphthoquinonediazide-4-sulfonate, 1, a 2-naphthoquinonediazide-5-sulfonate, The sulfonate of a quinone diazide derivative like a 2, 1-naphthoquinonediazide-4-sulfonate, 2, and 1-benzoquinone diazido-5-sulfonate, and 1, 2-benzoquinone-2-diazido-4-sulfonic-acid chloride, 1,2-naphthoquinone-2-diazido-4-sulfonic-acid chloride, 1,2-naphthoquinone-2-diazido-5-sulfonic-acid chloride, The sulfonic-acid chloride of quinone diazide derivatives, such as 1,2-naphthoquinone-1-diazido-6-sulfonic-acid chloride, 1, and 2-benzoquinone-1-diazido-5-sulfonic-acid chloride, etc. is mentioned.

[0014] As alpha and an alpha screw (sulfonyl) diazomethane system compound, alpha, alpha screw (sulfonyl) diazomethane, etc. which have un-permuting, the alkyl group permuted symmetrically or asymmetrically, an alkenyl radical, an aralkyl radical, an aromatic series radical, or a heterocycle-like radical are mentioned. As an example of an alpha-carbonyl-alpha-sulfonyl diazomethane system compound, the alpha-carbonyl-alpha-sulfonyl diazomethane which has un-permuting, the alkyl group permuted symmetrically or asymmetrically, an alkenyl radical, an aralkyl radical, an aromatic series radical, or a heterocycle-like radical is mentioned. As an example of a sulfone compound, a sulfone compound, a disulfon compound, etc. which have un-permuting, the alkyl group permuted symmetrically or asymmetrically, an alkenyl radical, an aralkyl radical, an aromatic series radical, or a heterocycle-like radical are mentioned.

[0015] As organic-acid ester, carboxylate, a sulfonate, phosphoric ester, etc. are mentioned, as an organic-acid amide, carboxylic amide, a sulfonic-acid amide, a phosphoric-acid amide, etc. are mentioned, and carboxylic-acid imide, sulfonic-acid imide, phosphoric-acid imide, etc. are mentioned as organic-acid imide.

[0016] These PAG may be used independently, or two or more kinds may be mixed and used for it. the resin 100 weight section which uses the loadings of these PAG by this invention -- receiving -- a minimum -- usually -- the 0.01 weight section -- desirable -- the 0.2 weight section -- it is -- an upper limit -- usually -- 50 weight sections -- they are 30 weight sections preferably. Formation of a pattern is an impossible next door under in the 0.01 weight section. If 50 weight sections are exceeded, that it is easy to generate ******, it will become or the problem of a pattern configuration getting worse will arise, and also when it is any, it is not desirable on the engine performance of a resist.

[0017] In this invention, it is made to dissolve in a solvent and the resist constituent which consists of said resin and PAG is used. What is generally used as a solvent for resist constituents can be used for a solvent. As an example Ketones; n-propanol, such as an acetone, a methyl ethyl ketone, a cyclohexanone, and cyclopentanone, i-propanol, n-butanol, i-butanol, t-butanol, Alcohols, such as a cyclohexanol; Ethylene glycol wood ether, Ether, such as ethylene glycol diethylether and dioxane; Ethylene glycol wood ether, Ethylene glycol monoethyl ether, propylene glycol monomethyl ether, Alcoholic ether, such as the propylene glycol monoethyl ether; Formic-acid propyl, Formic-acid butyl, propyl acetate, butyl acetate, methyl propionate, ethyl propionate, Ester; alpha-oxy-methyl propionates, such as methyl butyrate and ethyl butylate, alpha-oxy-ethyl propionate, 2-methoxy methyl propionate, Hydroxy acid ester, such as 2-methoxy ethyl propionate; A cellosolve acetate, Methyl-cellosolve acetate, ethylcellosolve acetate, a propyl cellosolve acetate, Cellosolve ester, such as butyl-cellosolve acetate; Propylene glycol, Propylene-glycol-monomethyl-ether acetate, propylene glycol monoethyl ether acetate, Propylene glycols, such as the propylene glycol monobutyl ether; The diethylene GIRIKORU monomethyl ether, Diethylene glycol monoethyl ether, diethylene-glycol wood ether, diethylene-glycols [, such as diethylene-glycol diethylether,], -- halogenated hydrocarbon [, such as a trichloroethylene,]; -- toluene -- Aromatic hydrocarbon, such as a xylene; polar solvents, such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl acetamide, and N-methyl pyrrolidone, etc. are illustrated, and these may mix and use independent or two kinds or

more.

[0018] An additive with compatibility, such as what is generally added by the resist constituent as an additive, for example, a surfactant, a preservation stabilizer, a sensitizer, a striae SHON inhibitor, and a low-molecular phenolic compound, can be made to contain in this invention.

[0019] In the constituent of this invention, the solubility of an irradiated part changes in response to an operation of the acid which generates the polymer which has the configuration unit expressed with said formula (3) from an acid generator by the exposure of a radiation. The constituent of this invention acts as a positive resist by using an alkali developer. By making the structural unit expressed with a formula (1) and (2) exist in a polymer, resist properties, such as dry cleaning-proof dirty nature, light transmission nature, definition, and the dissolution suppression effectiveness, improve.

[0020] Although the resist constituent of this invention usually uses an alkali water solution as an alkali developer As an example, a sodium hydroxide, a potassium hydroxide, a sodium silicate, The water solution of inorganic alkali, such as ammonia; The water-solution; diethylamine of primary amines, such as ethylamine and propylamine, The water solution of secondary amines, such as a dipropyl amine; The water-solution; diethyl ethanolamine of tertiary amines, such as a trimethylamine and triethylamine, The water solution of alcoholic amines, such as triethanolamine; Tetramethylammonium hydroxide, Tetraethylammonium hydroxide, trimethyl hydroxymethyl ammonium hydroxide, The water solution of quaternary ammonium hydroxide, such as triethyl hydroxymethyl ammonium hydroxide and trimethylhydroxyethylammonium hydroxide, etc. is mentioned. Moreover, water-soluble organic solvents, such as a methanol, ethanol, propanol, and ethylene glycol, a surfactant, the dissolution retardant of resin, etc. can be added in the above-mentioned alkali water solution if needed.

[0021] After applying the resist solution made to dissolve the resist constituent of this invention in a solvent to substrate front faces, such as a silicon wafer, with a conventional method, the resist film can be formed by carrying out desiccation removal of the solvent. Especially as the method of application at this time, the object for prizes of the spin coating is carried out. Thus, as a source of exposure used for the obtained resist film by the exposure for making a pattern form, sources of ionizing radiation, such as far ultraviolet rays, KrF excimer laser light, an X-ray, and an electron ray, are mentioned. Furthermore, by heat-treating after exposure (after [exposure] BEKU), a deprotection reaction is made to end and improvement and stabilization of sensibility can be attained.

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EXAMPLE

[Example] The example of reference, a synthetic example, and an example are given to below, and this invention is explained to it still more concretely. In addition, the section in each example and % are weight criteria as long as there is no notice especially.

[0023] (Synthetic example 1) 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / t-butyl Methacrylate polymer ** polymerization process 4-vinyl phenol 72.1g (0.60 mols), t-butyl Methacrylate 17.1g (0.12 mols), azobisisobutyronitril 1.5g (0.009 mols) and dioxane 150ml were taught to the 500ml flask, and stirring was performed at 80 degrees C under the nitrogen air current for 20 hours. The obtained reaction mixture was supplied to the 5l. xylene, and the produced precipitation was filtered. The obtained solid content was dissolved in diethylether 200ml, it supplied to 3l. n-hexane and the produced precipitation was filtered (reprecipitation actuation). After repeating this reprecipitation actuation 3 times, it dried and 26.3g 4-hydroxystyrene / t-butyl methacrylate polymer were obtained. The obtained polymer was Mw=5,130 as a result of GPC analysis. Moreover, the polymerization ratio of 4-hydroxystyrene / t-butyl methacrylate was 71/29 as a result of 1 H-NMR spectrum analysis.

[0024] ** 4-hydroxystyrene / 20.0g [of t-butyl methacrylate polymers], and acetone 150ml obtained by the qualification process point was taught and dissolved in 500ml flask. Bromoacetic acid 1-adamanthyl 6.2g (0.023 mols), 3.5g (0.025ml) of anhydrous potassium carbonate, and 4.2g (0.025 mols) of potassium iodide were added to this, and stirring was performed at 50 degrees C for 8 hours. After removing salts from the obtained reaction mixture, it supplied to 5l. n-hexane and the produced settling were filtered. The obtained solid content was dissolved in tetrahydrofuran 100ml, it supplied to the 5l. hexane and the produced precipitation was filtered (reprecipitation actuation). It dries, after repeating this reprecipitation actuation twice, and they are 18.8g 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / t-butyl. The methacrylate polymer was obtained. The obtained polymer was Mw=6,200 as a result of GPC analysis. Moreover, they are 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / t-butyl as a result of 1 H-NMR spectrum analysis. The polymerization ratio of methacrylate was 15/57/28.

[0025] (Synthetic example 2) 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / 1-methylcyclohexyl Methacrylate polymer ** polymerization process t-butyl It is 1-methylcyclohexyl instead of methacrylate. Except being referred to as methacrylate 29.1g (0.16 mols), it carried out like ** polymerization process of the synthetic example 1, and 22.7g 4-hydroxystyrene / 1-methylcyclohexyl methacrylate polymer were obtained. The obtained polymer was Mw=6,330 as a result of GPC analysis. Moreover, they are 4-hydroxystyrene / 1-methylcyclohexyl as a result of 1 H-NMR spectrum analysis. The polymerization ratio of methacrylate was 65/35.

** 4-hydroxystyrene / 1-methylcyclohexyl obtained at said process as a qualification process polymer Except using methacrylate 20.0g, it carries out like ** qualification process of the synthetic example 1, and they are 18.0g 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / 1-methylcyclohexyl. The methacrylate polymer was obtained. The obtained polymer was Mw=7,300 as a result of GPC analysis. Moreover, they are 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / 1-methylcyclohexyl as a result of 1 H-NMR

spectrum analysis. The polymerization ratio of methacrylate was 14/50. [0026] (Synthetic example 3) 4-(1-adamanthyl OKISHISHI carbonyl methyloxy) styrene / 4-hydroxystyrene / 3-methyl-2-butene Methacrylate polymer ** polymerization process t-butyl It is 3-methyl-2-butene instead of methacrylate. Except being referred to as methacrylate 18.5g (0.12 mols), it carried out like ** polymerization process of the synthetic example 1, and 20.7g 4-hydroxystyrene / 3-methyl-2-butene methacrylate polymer was obtained. The obtained polymer was Mw=5,500 as a result of GPC analysis. Moreover, they are 4-hydroxystyrene / 3-methyl-2-butene as a result of 1 H-NMR spectrum analysis. The polymerization ratio of methacrylate was 75/25.

** 4-hydroxystyrene / 3-methyl-2-butene obtained at said process as a qualification process polymer Except using methacrylate 20.0g, it carries out like ** qualification process of the synthetic example 1, and they are 19.0g 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / 3-methyl-2-butene. The methacrylate polymer was obtained. The obtained polymer was Mw=6,400 as a result of GPC analysis. Moreover, they are 4-(1-adamantyloxy carbonyl methyloxy) styrene / 4-hydroxystyrene / 3-methyl-2-butene as a result of 1 H-NMR spectrum analysis. The polymerization ratio of methacrylate was 16/59/25.

[0027] (Examples 1-4) The triphenylsulfonium triflate 5 section and the fluorochemical surfactant 0.01 section were dissolved in the ethyl lactate 440 section as the polymer 100 section obtained in the above-mentioned synthetic examples 1-3, and an acid generator, it filtered with the 0.1-micrometer filter made from polytetrafluoroethylene (Millipore Corp. make), and the resist solution was prepared. After carrying out the spin coat of this resist solution on a silicon wafer, the resist film of 1.0 micrometers of thickness was formed by performing BEKU for 90 seconds at 110 degrees C. This wafer was exposed using REKUCHIRU for a test with the KrF excimer stepper (NA=0.45). Subsequently, after performing BEKU for 60 seconds at 90 degrees C, the tetramethylammonium hydroxide water solution performed the immersion phenomenon for 1 minute, and the positive type pattern was obtained. Definition when the good pattern obtained by fitness-ization of the sensibility of these resist film and exposure is shown is shown in Table 1. Furthermore, when the wafer by which pattern formation was carried out was etched using the dry etching system (the product made from Japanese ** Anelva, DEM451T) by power 300W, pressure 0.03Torr, gas CF₄/H₂, and frequency 13.56MHz, with the wafer using the polymer of the synthetic examples 1-3, it turned out that only the place which did not have a pattern is etched. Moreover, observation of the resist pattern after etching was maintaining the configuration before etching mostly.

[0028]

[Table 1]

実施例	樹脂		感度 (mJ/cm ²)	解像性 (μm)
	合成例	k / m / n		
1	1	15/57/28	0.208	1.7 0.25
2	2	14/50/36	0.219	1.9 0.25
3	3	16/59/25	0.213	2.0 0.25

[Translation done.]

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